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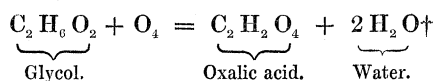
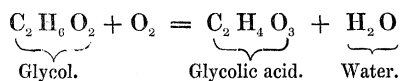
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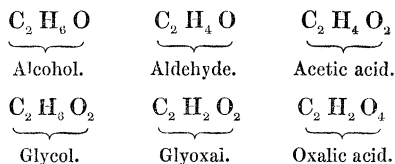
III. "On the Oxidation of Glycol, and on some Salts of Glyoxylic Acid." By H. DEBUS, Ph.D. Communicated by Dr. TYNDALL. Received March 16, 1859.

(Abstract.)

If glycol be oxidized with nitric acid, according to Wurtz\*, it is converted into glycolic and oxalic acids.



As the formation of these acids from glycol is analogous to the production of acetic acid from ethylic alcohol, it may be assumed that the bibasic oxalic acid stands to the biatomic glycol in the same relation as the fatty acids do to their corresponding alcohols. Alcohol is not converted at once into acetic acid, an intermediate substance—aldehyde—being formed. The formation of a similar body from glycol is highly probable. If two or four atoms of hydrogen be removed from glycol, an aldehyde of the composition of acetic acid or of the formula  $\text{C}_2\text{H}_2\text{O}_2$  may be produced. Glyoxal, obtained by the oxidation of ethylic alcohol, has indeed the composition corresponding to the above formula and the characteristic properties of an aldehyde. Nitric acid converts it rapidly into oxalic acid. Consequently glycol, glyoxal, and oxalic acid bear a similar relation to each other as ethylic alcohol, aldehyde, and acetic do.



Another connexion between glycol and glyoxal is that they both produce glycolic acid, the former by oxidation, and the latter by combi-

\* Comp. Rend. xliv. 1306.

† C=12, H=1, O=16.

nation with one atom of water. I treated glycol, which was diluted with water, with fuming nitric acid at about  $30^{\circ}\text{C.}$ , and evaporated the acid liquid, as soon as the action was completed, on the water-bath until it assumed the consistency of syrup\*. This residue was found to contain, as previously shown by Wurtz, oxalic and glycolic acids; but I also found therein glyoxylic acid and a body which comported itself with some reagents like glyoxal. Want of material, however, prevented its being identified with the latter.

Before I proceed to make some observations on these facts, I shall first mention a few salts of glyoxylic acid not yet described.

*Glyoxylate of silver*,  $\text{C}_2\text{HAgO}_3 + \text{H}_2\text{O}$ ,

is obtained as a white crystalline powder when nitrate of silver is precipitated with glyoxylate of ammonia. This salt is but slightly soluble in cold water, and is decomposed by light with great rapidity.

*Glyoxylate of baryta*,  $\text{C}_2\text{HBaO}_3 + 2\text{H}_2\text{O}$ .

Diluted glyoxylic acid is digested at common temperatures with carbonate of baryta until the acid is completely neutralized, and the filtered solution evaporated *in vacuo*. As soon as the liquid has arrived at a certain degree of concentration, small white crystals of glyoxylate of baryta begin to separate. This compound is partially decomposed into oxalate of baryta and glycolic acid if it be heated to  $120^{\circ}\text{C.}$ , or if the temperature of its watery solution be raised to the boiling-point. With nitrate of silver, acetate of lead, and lime-water, it comports itself like glyoxylate of lime.

*Glyoxylate of zinc*,  $\text{C}_2\text{Zn}_2\text{O}_3 + 2\text{H}_2\text{O}$ ,

is produced as a white crystalline precipitate when a strong solution of glyoxylate of lime is precipitated with acetate of zinc. This compound is slightly soluble in water, but is easily dissolved by acetic and hydrochloric acids and by caustic potash. The two atoms of water cannot be removed without decomposing the salt.

*Glyoxylate of ammonia*,  $\text{C}_2\text{H}(\text{NH}_4)\text{O}_3$ .

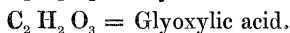
This compound was prepared by precipitating glyoxylate of lime with its equivalent quantity of oxalate of ammonia, and evaporating

\* "On the Action of Nitric Acid on Alcohol," Phil. Mag. Jan. 1857; Ann. der Chem. und Pharm. cii. 26.

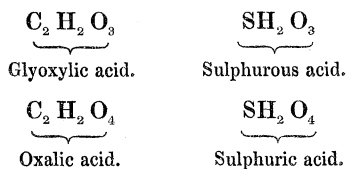
the filtrate from the oxalate of lime over sulphuric acid *in vacuo*. The glyoxylate of ammonia is obtained in small, prismatic and colourless crystals, which dissolve easily in water. The concentrated solution turns yellow when it is boiled, or evaporated at 100° C. It produces with nitrate of silver and acetate of lead crystalline precipitates at once, but with sulphate of copper only after the lapse of some time. Solution of caustic potash, mixed with it, causes the evolution of ammonia even at common temperatures.

According to the composition of glyoxylate of ammonia, the formula of glyoxylic acid is  $C_2 H_2 O_3^*$ . It is worthy of notice, that the other salts of this acid which have been examined, contain one or two atoms of water which cannot be expelled without decomposing the compound.

Glyoxal is oxidized, by treatment with dilute nitric acid, into oxalic acid, and as an intermediate substance glyoxylic acid is formed.



Glyoxal has not been proved with certainty to be one of the products of the oxidation of glycol; nevertheless its formation from this alcohol may be foreseen with great probability, as it stands to glyoxylic and oxalic acids, both of which are formed by the oxidation of glycol, as ethylic aldehyde does to acetic acid. The relation of glyoxylic to oxalic acid is like that of sulphurous to sulphuric acid.

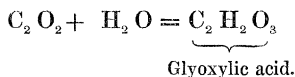
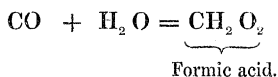


Glyoxylic acid resembles in many respects formic acid. Concentrated sulphuric acid separates from the salts of formic acid carbonic oxide, whilst it combines with the rest of the constituents. Glyoxylate of lime dissolves in an excess of sulphuric acid, and the solution evolves at a temperature of from 40° to 50° C., without blackening, pure carbonic oxide. At the end of the experiment, and when the

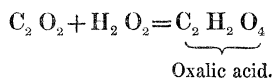
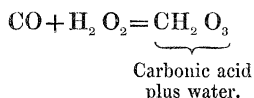
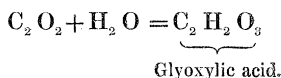
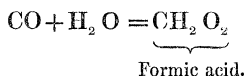
\* "On Glyoxal," Phil. Mag. Jan. 1857; Ann. der Chem. und Pharm. cii. 29.

temperature of the liquid is raised, a little sulphurous acid makes its appearance.

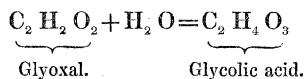
Relying on Berthelot's experiments, formic acid we can conceive to be formed by the addition of the molecule carbonyl to the type water. In the same manner glyoxylic acid might be produced by adding oxalyle to one atom of water.



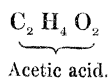
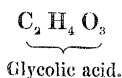
Since both acids are easily oxidized, the one to carbonic, and the other to oxalic acid, we may say that, with regard to composition, formic acid stands to carbonic acid in a similar relation as glyoxylic acid does to oxalic acid.



But with regard to other properties, these acids do not correspond to each other: thus formic acid is monobasic and carbonic acid bibasic, whilst both glyoxylic and oxalic acids are biatomic. Further, the latter two are derived from the same alcohol, which is not the case with carbonic and formic acids. Amongst the products of the oxidation of glycol occurs also glycolic acid, which is produced from glyoxal by the assimilation of water.

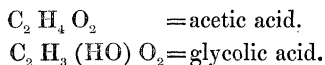


Some regard glycolic acid ( $\text{C}_2\text{H}_4\text{O}_3$ ) as a bibasic acid. According to this view, it would stand to glycol as acetic acid does to common alcohol.



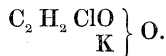
But with this view the capacity of saturation of glycolic acid does not agree. For according to our present experience, if we adopt the formula  $C_2 H_4 O_3$ , it evidently combines only with one atom of base. Before we have discovered compounds represented by the general expression  $C_2 H_2 M_2 O_3$ , I think we are not justified to place glycolic acid in the same relation to glycol as we do acetic acid to common alcohol. According to our present knowledge, this position must be assigned to oxalic acid.

We can represent to our minds the derivation of glycolic acid from acetic acid in the following manner. If in acetic acid one atom of hydrogen be replaced by peroxide of hydrogen, we obtain a body which has the composition of glycolic acid.

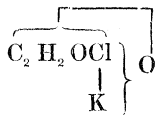


But, according to the following observations, this view appears not to be correct; for glycolic acid can be formed from glycolide and water, and probably also again can be resolved into these two substances in the same way as lactid and water by their union produce lactic acid, and the decomposition of the latter by heat yields lactid again. If, therefore, peroxide of hydrogen be contained in glycolic acid, it must be present in glycolide.

If monochlorinated acetate of potash be decomposed, according to Kekule, glycolic acid and glycolide are formed. The formation of the latter precedes that of the glycolic acid; but if the monochlorinated acetate of potash could be obtained anhydrous, no doubt only glycolide would result from its decomposition. The monochlorinated acetate of potash can be represented as consisting of three parts,—of potassium, of oxygen, and of chlorinated acetylene.

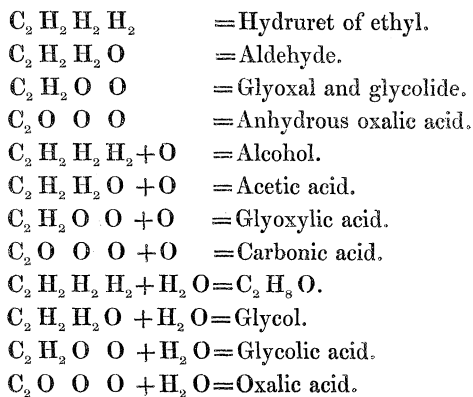


At a higher temperature chlorine and potassium form chloride of potassium. After the removal of the chlorine, the chlorinated acetylene is converted into the biatomic radical  $C_2 H_2 O$ , which unites with one atom of oxygen, and forms glycolide.



According to its formation, the glycolide cannot contain any peroxide of hydrogen, and consequently it appears that also glycolic acid cannot be considered as acetic acid wherein one atom of hydrogen has been replaced by peroxide of hydrogen.

I beg to conclude with an empirical derivation of several of the compounds mentioned from hydruret of ethyl.



*April 7, 1859.*

Sir BENJAMIN C. BRODIE, Bart., President, in the Chair.

The following communications were read:—

- I. "On Colour-Blindness." By WILLIAM POLE, Esq. Communicated by Professor STOKES, Sec.R.S. Received March 24, 1859.

This paper consists principally of a revised and condensed version of a former one by the same author, which was read to the Society on the 19th of June, 1856, and of which an abstract is given in the 'Proceedings' under that date (vol. viii. p.172). In the present communication there is added an account of numerous experiments subsequently made by the author with Professor Maxwell's Colour-top.